John von Neumann Institute for Computing

Interaction of Biological Matter with Nanomaterials: A First-Principles Approach

S. Gowtham, R. H. Scheicher, R. Ahuja, R. Pandey

published in

From Computational Biophysics to Systems Biology (CBSB07),
Proceedings of the NIC Workshop 2007,
Ulrich H. E. Hansmann, Jan Meinke, Sandipan Mohanty,
Olav Zimmermann (Editors),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. **36**, ISBN 978-3-9810843-2-0, pp. 117-120, 2007.

http://www.fz-juelich.de/nic-series/volume36

Interaction of Biological Matter with Nanomaterials: A First-Principles Approach

S. Gowtham[1], Ralph H. Scheicher[1], Rajeev Ahuja[2], and Ravindra Pandey[1]

[1] Department of Physics, Michigan Technological University, Houghton, MI USA
E-mail: sgowtham@mtu.edu

[2] Condensed Matter Theory Group, Department of Physics, Uppsala University, Uppsala, Sweden
Applied Materials Physics, Department of Materials and Engineering,
Royal Institute of Technology, Stockholm, Sweden

1 Introduction

DNA-coated carbon nanotubes represent a hybrid system which unites the biological regime and the nanomaterials world. They possess features which make them attractive for a broad range of applications, e.g., as an efficient method to separate carbon nanotubes (CNTs) according to their electronic properties[1–3], as highly specific nanosensors, or as an in vivo optical detector for ions. It has also been experimentally demonstrated that ssDNA can be inserted into a CNT[5], further enhancing the potential applications of this nano-bio system. Our specific interest is to assess the subtle differences in the adsorption strength of these nucleobases on graphene, which in turn will allow us to draw conclusions for the interaction of DNA and RNA with CNTs as well.

2 Computational Method

Calculations were performed using the plane-wave pseudopotential approach within the local density approximation (LDA)[6] of density functional theory (DFT)[7], as implemented in the Vienna Ab-initio Simulation Package (VASP)[8].

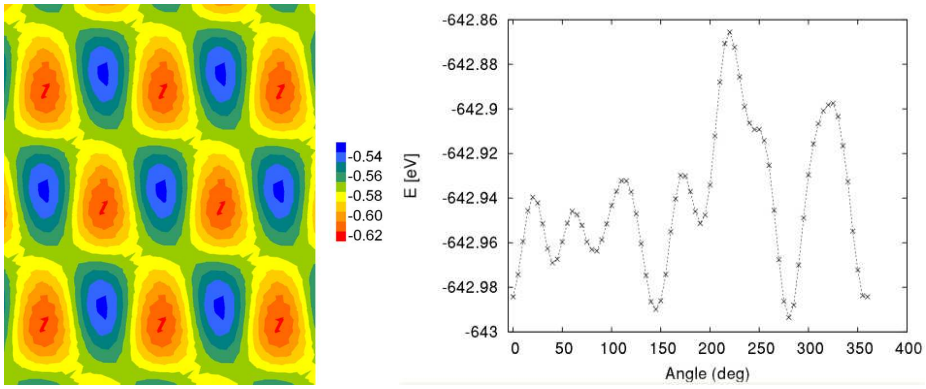
A 5×5 array of the graphene unit cell in the x-y plane and a separation of 15 Å between adjacent graphene sheets in the z-direction was found to be a suitable choice to represent the supercell. The base molecules were terminated at the cut bond to the sugar ring with a methyl group in order to generate an electronic environment in the nucleobase more closely resembling the situation in DNA and RNA rather than that of just individual isolated bases by themselves.

For each of the five nucleobases, an *initial force relaxation* calculation step determined the preferred orientation and optimum height of the planar base molecule relative to the graphene sheet. The potential energy surface was then explored by translating the relaxed base molecules parallel to the graphene plane in steps of 0.246 Å along the lattice vectors of graphene, covering its entire unit cell by a mesh of 10×10 scan points. The determination of the minimum total energy configuration was then followed by a 360° rotation of the base molecules in steps of 5° to probe the dependence of the energy on the orientation of the base molecules with respect to the underlying 2-D graphene sheet. The configuration yielding the minimum total energy was used in the final optimization step in which all atoms in the system were free to relax.

3 Results and Discussion

From the optimization steps involving the translational and the rotational scan of the energy surface, it is apparent that the energy barriers to lateral movement and to rotation of a given base can range from 0.04 to 0.10 eV (Fig. 1(a)), thus considerably affecting the mobility of the adsorbed nucleobases on the graphene sheet at room temperature, and constricting their movement to certain directions.

In their equilibrium configuration, all five bases tend to position themselves on graphene in a configuration reminiscent of the Bernal's AB stacking of two adjacent graphene layers in graphite (Fig. 2). Virtually no changes in the interatomic structure of the nucleobases were found in their equilibrium configurations with respect to the corresponding gas-phase geometries, as it could be expected for a weakly interacting system such as the one studied here. A notable exception is the R_{C-O} in guanine which shows a 10% contraction upon physisorption of the molecule on graphene.



(a) Surface Scan (b) Rotation Scan

Figure 1. Potential energy surface (PES) plot (in eV) for guanine on graphene. Qualitatively similar PES plots were obtained for the other four nucleobases.

The binding energy of the system consisting of the nucleobase and the graphene sheet is taken as the energy of the equilibrium configuration with reference to the asymptotic limit obtained by varying the distance between the base and the graphene sheet in the z-direction (Table 1). This table also includes the polarizabilities of the nucleobases calculated at the MP2 level of theory. The polarizability of the nucleobase[9], which represents the deformability of the electronic charge distribution, is known to arise from the regions associated with the aromatic rings, lone pairs of nitrogen and oxygen atoms. Accordingly, the purine base guanine appears to have the largest value, whereas the pyrimidine base uracil has the smallest value among the five nucleobases. Our calculations confirm this behavior.

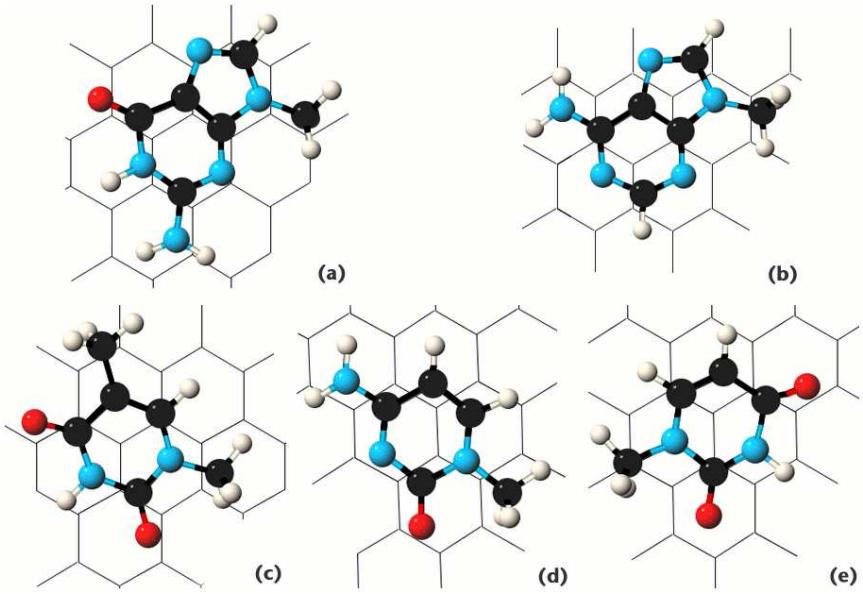


Figure 2. Equilibrium geometry of nucleobases on top of graphene: (a) guanine, (b) adenine, (c) thymine, (d) cytosine, and (e) uracil.

Base	E_b(LDA) [eV]	E_b(MP2) [eV]	α $[e^2 a_0^2 E_h^{-1}]$
G	0.61	1.07	131.2
A	0.49	0.94	123.7
T	0.49	0.83	111.4
C	0.49	0.80	108.5
U	0.44	0.74	97.6

Table 1. Binding energy E_b of the DNA/RNA nucleobases with graphene as calculated within LDA are compared with binding energy and polarizability α from MP2 calculations.

4 Conclusions

Our first-principles results clearly demonstrate that the nucleobases exhibit significantly different interaction strengths when physisorbed on graphene. This finding represents an important step towards a better understanding of experimentally observed sequence-dependent interaction of DNA with CNTs[3,4]. The calculated trend in the binding energies strongly suggests that the polarizability of the base molecules determines the interaction strength of the nucleobases with graphene. Further studies involving the investigation of nucleobases interacting with small-diameter CNTs are currently underway.

Acknowledgments

S.G., R.H.S., and R.P. would like to thank DARPA for funding. Authors are grateful to Center for Experimental Computation at MTU and the Swedish National Infrastructure (SNIC) for computing time.

References

1. N. Nakashima *et al.*, Chem. Lett. **32**, 456 (2003).
2. M. Zheng *et al.*, Nature Mater. **2**, 338 (2003).
3. M. Zheng *et al.*, Science **302**, 1545 (2003).
4. C. Staii *et al.*, Nano Lett. **5**, 1774 (2005).
5. T. Okada *et al.*, Chem. Phys. Lett. **417**, 288 (2006).
6. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
7. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
8. G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
9. Frank Seela, Anup M. Jawalekar, and Ingo Münster, Helevetica Chimica Acta **88**, 751 (2005).